Abstract

In this work, novel heterostructured uranium oxide materials were tested for solar energy conversion via photoelectrochemical water splitting. Uranium oxides with band-gap energies in the range of 1.8-3.2 eV coupled with their good electrical and catalytic properties mostly driven by facile valence dynamics of the uranium cations are promising electrode materials for this application. Although being considered a scarce element, huge amounts of depleted uranium sources (e.g. alone 700,000 tons UF_6 dumped in the USA) originally produced as waste streams in the enrichment process of nuclear fuels, are currently stored without any prospect for further applications. That poses a perpetual environmental hazard, due to accidental release of volatile, corrosive and toxic compounds. Although exhibiting interesting electronic and structural properties, (depleted) uranium oxides have not been probed so far as materials for energy applications due to their limited synthetic accessibility. For the first time, a range of uranium metal-organic precursors have been synthesized and probed in the gas phase deposition (thermal and plasma-enhanced chemical vapor deposition) of uranium oxide coatings. It was demonstrated that the phase composition of resulting CVD deposits depended to a large extent on the oxidation state of the uranium center as well as on the configuration of ligands. The resulting thin films of uranium oxides have been investigated as potential photoelectrodes in water splitting setups. Preliminary studies illustrate the enormous and mostly unexplored potential of UO_x compounds in (photo)chemical energy conversion cycles. Compared to well-known semiconductor metal oxides such as TiO_2, Fe_2O_3 and ZnO, the chemistry and materials aspects of uranium oxides are scantily explored and therefore this effort was accompanied by *ab-initio* DFT calculations to understand the underlying processes with respect to water splitting reactions. In addition, the influence of the U:O ratio on the band gap energies as well the thermodynamic stability of UO_x with other potential photoanode materials was investigated by theoretical studies as well as by oxygen *K*-edge X-ray absorption spectroscopy (XAS). Furthermore, the effect of impurities (dopants) and interface modification via fabrication of UO_x/MO_x (M = Fe, Ti, Zr, W) bilayered heterostructures were elaborated via *in-situ* XAS and transient absorption spectroscopy (TAS) for a detailed understanding of the photoelectrocatalytic performance and the assessment of the beneficial use of uranium oxide in solar-driven water splitting applications.